

Random coupling model for multiphoton photofragmentation of large molecules

Israel Schek and Joshua Jortner

Department of Chemistry, Tel-Aviv University, Tel Aviv, Israel
(Received 14 September 1978)

In this paper we present a quantum mechanical theory of multiphoton photodissociation of large, collision-free, molecules, which rests on the notion that the radiative coupling terms between adjacent sets of congested bound molecular states in the quasicontinuum exhibit a wide variation both in terms of magnitude and of sign. Invoking the rotating-wave approximation, neglecting spontaneous infrared decay, and assuming that near-resonant radiative coupling prevails, the equations of motion were solved within the framework of the random radiative coupling model for the radiative interactions in the quasicontinuum. In the low energy range (range I) the equations of motion for the amplitudes are determined by the effective Hamiltonian formalism, while in the quasicontinuum (range II) the populations are governed by kinetic equations for sequential reversible decay. All the features of coherent excitation are preserved for range I, while in range II intramolecular erosion of phase coherence effects prevails. This model provides a set of reasonable predictions.

I. INTRODUCTORY REMARKS

The experimental observation¹⁻¹⁷ of multiphoton photofragmentation of collision-free polyatomic molecules is of considerable current interest.¹⁷⁻³⁰ To elucidate the gross features of these high-order multiphoton molecular processes it is convenient to divide the level structure into three energy regions, in the order of increasing energy.^{18,22} Range I corresponds to a sparse level distribution of bound molecular states. The gross features of range I involve a discrete spectrum with near-resonant radiative interactions, which results in a coherent, phase-preserving, multiphoton excitation. The notable experimental consequences of the high-order excitation of range I^{15,18,22,25,26,30} involve the isotopic selectivity, the power dependence of the excitation yield, together with the occurrence of saturation effects in a discrete near-resonance spectrum, as well as the appearance of multiphoton resonances. Range II constitutes the intermediate energy range which is characterized by a dense level distribution of bound states. When the density of the bound nuclear levels is high, all zero-order descriptions of the energy levels become inadequate and the only appropriate description is provided in terms of the nuclear molecular eigenstates (NMEs).³¹ These energy levels correspond to the eigenstates of the molecular nuclear Hamiltonian. Although the NMEs are not known at present for any polyatomic molecule, they constitute a basic theoretical framework for the study of intramolecular dynamics in large molecules. The onset of range II can be characterized by two conditions: (a) A physical irreversibility condition²² implying the overlap of resonances originating from infrared decay, i.e., $\gamma_m^{\text{IR}} \rho(E) > 1$, where γ_m^{IR} is the infrared decay width of the NME $|m\rangle$, while $\rho(E)$ corresponds to the density of states of the NMEs; (b) A practical condition for irreversibility³¹ in a discrete congested level structure implying that $T_e < \hbar \rho(E)$, where T_e is the upper limit for the time scale of the experiment. For the celebrated SF₆ molecule, condition (a) implies that for $E > 10^4$ cm⁻¹ the quasicontinuum acts as a real physical continuum, while from condition (b) one can infer that for a time scale of $T_e \sim 100$ nsec practical irreversibility is obeyed for $E > 5000$ cm⁻¹. Once the general point of view, which

rests on the notion of NMEs, is accepted one can essentially evade the issues of intramolecular vibrational relaxation (IVR)^{15,18,30} and of the energy redistribution in a large molecule undergoing multiphoton excitation. Obviously, once a packet of NMEs (corresponding to some zero-order state) is "initially excited" under well-defined experimental conditions, it is legitimate to probe the dynamics of the IVR process. However, in the present case of a high-order multiphoton process one has to consider the implications of a resonant radiative coupling in the congested bound level structure of range II and we would like to argue that the notion of IVR is irrelevant for the problem at hand. Finally, range III located above the first dissociation threshold corresponds to the reactive region.

While the characteristics of range I in large molecules were quite extensively studied by the application of the effective Hamiltonian formalism and are reasonably well understood, the nature of range II and the physical implications of radiative coupling with such a molecular quasicontinuum constitute an interesting problem to which we shall address ourselves in the present paper. In this context Bloembergen and colleagues^{15,18} invoked the notion of IVR in range II, where successive absorption and stimulated emission of single photons were assumed to take place. Kolodner *et al.*¹¹ and Black *et al.*¹⁵ have demonstrated that provided that when the laser intensity is sufficiently high to overcome range I the photofragmentation yield is determined by the pulse energy, providing overwhelming evidence for the erosion of phase memory effects in range II. Thus for a large molecule, such as SF₆, incoherent excitation prevails in range II. Mukamel,³² Hodgkinson and Briggs,³³ and Cantrell *et al.*³⁰ have advanced a theoretical description of multiphoton excitation in range II of SF₆ by dividing the zero-order molecular energy levels into two parts. The "relevant" part consists of the ν_3 mode, while the "irrelevant" part consists of the vibrational quasicontinuum of all the other modes. These two subsystems are coupled by intramolecular anharmonic interactions. The time evolution of the system was handled by the equations of motion for the reduced density matrix,³⁴ where the vibrational quasicontinuum

plays the role of an intramolecular reservoir. It was argued by Mukamel³² and by Cantrell³⁰ that intramolecular anharmonic coupling results in erosion of phase coherence effects, resulting in a Markovian master equation for the small relevant subset of levels. A serious hidden assumption underlying this treatment involves the hypothesis of selective radiative coupling. Over the entire energy range II it is asserted^{30,33} that effective radiative coupling prevails only between the ν_3 states, while no radiative coupling occurs between high-energy reservoir states. This assumption is expected to break down at high vibrational energies. Furthermore, the anharmonic coupling terms are expected to become appreciable at high energies, rendering the harmonic basis useless. The segregation of the nuclear energy levels may be adequate only provided that the high vibrational overtones can be described in terms of local bond modes, as is the case for molecules containing X-H bonds.³⁵ This is not the case for multiphoton excitation of SF₆. We thus believe that the assumption of selective radiative coupling, which provides the basis for the level segregation procedure, is inadequate for a large molecule such as SF₆. We would like also to point out that Bloembergen's unimolecular model¹⁸ predicts that in most cases the multiphoton photodissociation process will result in the production of ground state fragments, while some (though by no means conclusive) evidence is available⁵ for the formation of electronically excited radicals, and recent experimental work¹⁴ demonstrates the production of electronically excited states of the parent molecule via multiphoton vibrational excitation. Further work is required to elucidate the nature of multiphoton excitation in range II and to establish the characteristics of chemical and photophysical processes in highly excited vibrational states of polyatomics. In this paper we shall consider a quantum mechanical model for multiphoton photodissociation of an "isolated" large molecule. This model rests on the notion of random radiative coupling within a congested manifold of bound states in range II. A preliminary exposition of the features of this model was already provided.³⁶ From the point of view of general methodology the random radiative coupling model does not invoke the controversial notion of IVR in a single molecule, but rather utilizes the NMEs as a proper ("exact") molecular basis set for the study of high-order multiphoton molecular processes. From the practical point of view this model is hopefully realistic and provides a set of predictions which are consistent with the experimental facts of life.

II. THE RANDOM RADIATIVE COUPLING MODEL

The novel and truly interesting feature of the problem of multiphoton photofragmentation of an isolated polyatomic molecule involves the nature of the excitation of the quasicontinuum of bound states. We shall advance a model for this problem attempting to utilize as input data just the relevant quantum mechanical "observables," i.e., the energies of the molecular bound levels and the multiphoton radiative coupling terms. Our starting point rests on the set of NMEs $\{|m\rangle\}$ states, which in ranges I and II are bound, constituting the eigenstates of the molecular Hamiltonian so that the only residual

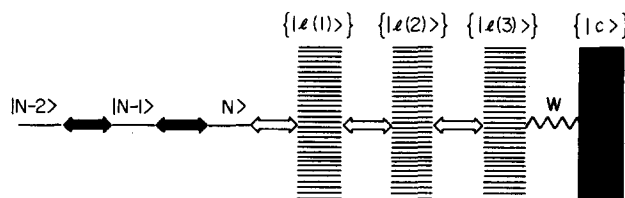


FIG. 1. Energy level diagram for the dressed states in the random coupling model. Black arrows correspond to radiative coupling, white arrows denote random radiative coupling terms, while the wiggly line represents the intramolecular coupling to the dissociative continuum.

coupling involves the radiative interactions. Range I (see Fig. 1) consists of a small number, N , of discrete states characterized by the molecular energies E_α ($\alpha = 1, 2, \dots, N$), which are well separated in energy, being near resonant with the laser frequency $\hbar\omega$. Range II consists of a series of Q dense molecular manifolds $\{|I(\beta)\rangle\}$ with energies $E_{I(\beta)}$, where $\beta = 1, 2, \dots, Q$ labels the particular dense manifold. Each of these discrete manifolds is in resonance with the laser energy $\hbar\omega$. Thus the minimum number of laser photons required for photodissociation is now $M - 1$, where $M = N + Q$. The photofragmentation process will be described by adding a single real continuum $\{|c\rangle\}$ to represent range III, the continuum state being characterized by the energies E_c . Each of the (discrete) states in the Q th dense manifold is coupled via nonadiabatic intramolecular coupling to the states in this dissociative continuum. Next, we turn to consider the laser field. An intense electromagnetic field will be specified in terms of a state $|n\rangle$ containing ($n \gg 1$) photons of frequency ω in a single mode, which is switched on the time scale $0 \leq t \leq T$. We note in passing that the results obtained for $n \gg 1$ (or rather for $n \gg M$) using the quantum description of the radiation field are equivalent to those derived by using a classical field.³⁷ The Hamiltonian for the problem will be expressed in the conventional form

$$H = H_0 + V + W, \quad (1)$$

$$H_0 = H_M + H_{\text{rad}},$$

where H_M is the molecular Hamiltonian, W the intramolecular coupling to the dissociative states, H_{rad} corresponds to the Hamiltonian of the radiation field, while V represents the radiation-matter interaction term, taken in a time-independent representation.

We shall now introduce three basic assumptions, which were previously utilized to derive the effective Hamiltonian formalism. First, the rotating wave approximation (RWA)³⁸ is invoked, allowing us to consider the time evolution of the "dressed" molecule-radiation³⁸ eigenstates of H_0 (Fig. 1). These correspond to the discrete, sparsely spaced, "dressed" states $|\alpha\rangle = |\alpha, n - \alpha + 1\rangle$ with energies $E(\alpha) = E_\alpha + (n - \alpha + 1)\hbar\omega$, ($\alpha = 1, \dots, N$) for range I, the Q dense manifolds of discrete states $\{|I(\beta)\rangle\} = |I(\beta), n - \beta - N + 1\rangle$ with energies $E(I(\beta)) = E_{I(\beta)} + (n - N - \beta + 1)\hbar\omega$, ($\beta = 1, \dots, Q$) for each state in range II, and the continuum states in range III correspond to $\{|c\rangle\} = \{|c, n - M + 1\rangle\}$ with energies $E(c) = E_c + (n - M + 1)\hbar\omega$. Second, we shall neglect spontaneous

infrared radiative decay. Third, we shall assume that effective radiative coupling prevails only between adjacent states in range I, between adjacent dense manifolds in range II, and between the $|N\rangle$ state and the $\{|I(1)\rangle\}$ manifold (Fig. 1). This assumption together with the RWA enables us to consider one set of dressed states, characterized by a single value of n . The time evolution of the system can be expressed in terms of the dressed states

$$\Psi(t) = \sum_{\alpha=1}^N a_{\alpha}(t) |\alpha\rangle + \sum_{\beta=1}^Q \sum_I a_{I(\beta)}(t) |I(\beta)\rangle + \sum_c a_c(t) |c\rangle, \quad (2)$$

with the initial condition $a_1(t=0) = 1$. In order to express the equations of motion we have to specify all the coupling terms. In ranges I and II these correspond to radiative interactions and will be denoted by

$$\langle \alpha | V | \alpha' \rangle = \mu_{\alpha\alpha'} \epsilon \delta_{\alpha', \alpha \pm 1} \quad (3a)$$

for range I

$$\langle N | V | I(1) \rangle = \mu_{N, I(1)} \epsilon; \quad \text{all } I(1) \quad (3b)$$

for the interaction between ranges I and II, as originally proposed by Letokhov and Makarov,²⁶ and

$$\langle I(\beta) | V | m(\gamma) \rangle = \mu_{I(\beta), m(\gamma)} \epsilon \quad \beta, \gamma = N+1, \dots, M \quad (3c)$$

$$|\beta - \gamma| = 1$$

for the coupling between states in the dense manifolds in range II. Here μ is the projection of the dipole operator in the direction of the field and ϵ denotes the magnitude of the electric field. Finally, for the interaction with range III we take

$$\langle I(Q) | W | c \rangle = W(I(Q), c). \quad (3d)$$

The equations of motion for the amplitudes in Eq. (2) are

$$i \frac{d\mathbf{a}}{dt} = (\mathbf{H}_0 + \mathbf{V} + \mathbf{W}) \mathbf{a}, \quad (4)$$

where \mathbf{a} is the vector of all the amplitudes and the matrices \mathbf{H}_0 , \mathbf{V} , and \mathbf{W} are expressed in the representation of the dressed states.

As is evident from Fig. 1, Eq. (4) represents the time evolution of a manifold of discrete states which are feeding a set of adjacently coupled quasicontinua which finally terminate by decay into the final continuum. The problem of a discrete state coupled to a manifold of adjacently coupled continua has been extensively studied in relation to the dynamics of a "conventional" one-photon induced photochemical process. Rice *et al.*³⁹ (RMJ), Lefebvre and Beswick,⁴⁰ and Nitzan *et al.*⁴¹ have explored the sequential decay problem where the intercontinuum coupling is a smooth weakly varying function of energy. The decay pattern is dominated by interference effects, which result in the retardation of the decay of the discrete state and in a simultaneous population of all continua. This physical picture has been recently utilized in the theories of (one-photon) molecular photofragmentation⁴² and vibrational predissociation of van der Waals molecules.⁴³ Another extreme involves the sequential decay model when each state decays into its own, private, continuum. Nitzan *et al.*⁴⁴ (NJR) have demonstrated that the sequential decay model obeys conven-

tional kinetic equations. The relation between RMJ³⁹ and the NJR⁴⁴ models was investigated by Heller and Rice,⁴⁵ Kay,⁴⁶ and Tric,⁴⁷ who invoked the assumption of random coupling in the RMJ model deriving a set of kinetic equations for sequential decay. However, as recently shown by Carmeli and Nitzan,⁴⁸ the Heller-Rice solution⁴⁵ is restricted to the case of a low density of states in the intermediate continuum. Carmeli and Nitzan⁴⁸ extended the Heller-Rice treatment⁴⁵ of separable random coupling for the RMJ model which results in a two-way master equation. It is now well established that random coupling effects result in erosion of interference effects,^{44-48,36} whereupon phase coherence phenomena can be washed out.

The sequential coupling models with interference³⁹⁻⁴³ are obviously inappropriate for the problem of multiphoton photodissociation as this model requires that the coupling terms between the quasicontinua be "smooth," being weakly varying with energy. The radiative coupling terms $V_{N, I(1)} = \mu_{N, I(1)} \epsilon$ for the interaction between the bound state and the quasicontinuum and $V_{I(\beta), m(\beta \pm 1)} = \mu_{I(\beta), m(\beta \pm 1)} \epsilon$ for the interaction between pairs of dense manifolds are expected to vary widely with respect both to magnitude and to sign between various matrix elements. We propose³⁶ that this variation of the radiative matrix elements can be described in terms of a random radiative coupling model and this lack of correlations in sign and in magnitude of the radiative coupling terms in the quasicontinuum will result in erosion of coherence effects in range II. We must now explore the consequences of the random radiative coupling on the intramolecular dynamics. The Heller-Rice model⁴⁵ as extended by Carmeli and Nitzan⁴⁸ is too restricted, as it rests on a separable interaction scheme. The conventional derivation which rests on a brute-force solution of the equations of motion for randomly coupled quasicontinua, Eq. (4), which was attempted before,³⁶ does not lead to a self-consistent solution.⁴⁹ The most promising avenue is to adopt the Wigner-Weisskopf approximation for range I, while in range II we shall adopt Kay's procedure⁴⁶ for random intercontinuum coupling.

To specify the nature of the random coupling terms we shall invoke a mathematical definition of randomness, asserting that the off-diagonal matrix elements of the level shift operator are considerably smaller than the corresponding diagonal terms. The complementary relations in the time domain for the coupling between continua are

$$\langle m(\gamma) | VA(\alpha)V | n(\delta) \rangle = \delta_{nm} \delta_{\gamma\delta} \langle m(\gamma) | VA(\alpha)V | m(\gamma) \rangle, \quad (5)$$

where

$$A(\alpha) = \sum_n |n(\alpha)\rangle e^{iE_n \alpha t} \langle n(\alpha) | \quad (6)$$

is a function of the eigenvalues of \mathbf{H}_0 . We also assume that the coupling between the highest N state and the quasicontinuum is random in the same sense,

$$\langle N | VA(\beta)V | I(\gamma) \rangle = 0. \quad (7)$$

This definition of randomness given in terms of Eqs. (5)-(7) for coupled quasicontinua bears a close analogy to the celebrated Van Hove diagonal singularity condi-

tion^{34a} for infinite systems. We now proceed to explore the implications of the random radiative coupling model (RRCM).

The mathematical manipulations involved in the derivation of the equations of motion in range I are similar to those utilized for the self-consistent derivation of the Wigner-Weisskopf approximation.³⁶ The time evolution of the amplitudes $a_1 \cdots a_{N-1}$ is given by Eq. (4). For the amplitude a_N of the highest dressed state in range I, we utilize Eq. (4) together with Condition (7) to get

$$i \dot{a}_N = \mu_{N,N-1} \epsilon a_{N-1} - (i \Gamma_N/2) a_N, \quad (8)$$

where

$$\Gamma_N = 2\pi \langle |\mu_{N,I(1)}|^2 \rho_{(1)} \rangle \epsilon^2 \quad (9)$$

is the width of the N th (discrete) state due to radiative coupling to the quasicontinuum. Here $\langle \rangle$ denotes averaging over the (random) $\{|I(1)\}$ manifold and $\rho_{(1)}$ is the density of states in this manifold. Thus the quasicontinuum provides an irreversible decay channel for the $|N\rangle$ state. This result is not surprising. However, it should be noted that the independence of Γ_N , Eq. (9), on the coupling in range II is a consequence of the random coupling assumption.

Next, we address ourselves to the central problem of the dynamics in range II. To consider the time evolution in range II it will be convenient to write the equations of motion for the density matrix

$$\begin{aligned} \rho_{I(\beta),m(\gamma)}(t) &= a_{I(\beta)}^*(t) a_{m(\gamma)}(t), \\ \rho_{N,m(\gamma)}(t) &= a_N^*(t) a_{m(\gamma)}(t), \end{aligned} \quad (10)$$

so that the population of the $|N\rangle$ state is $P_N(t) = \rho_{N,N}(t)$, while the entire population $P_{(\beta)}(t)$ of the dense manifold (β) is

$$P_{(\beta)}(t) = \sum_I \rho_{I(\beta),I(\beta)}(t). \quad (11)$$

For the sake of simplicity we shall now consider the dynamics of state N coupled to range II, disregarding for the moment the dissociative range III. The time evolution of the system over a period $t \cdots t + \tau$ is given in the conventional form

$$\Psi(t + \tau) = e^{-iH\tau} \Psi(t). \quad (12)$$

Utilizing Eqs. (1) and (10)–(12), simple manipulations result in the general relations

$$\begin{aligned} P_{(\beta)}(t + \tau) &= \sum_m \sum_n \sum_\gamma \sum_\beta I_{n(\beta),m(\gamma)}^{(\beta)}(\tau) \rho_{m(\gamma),n(\beta)}(t) \\ &+ \sum_m \sum_\gamma I_{N,m(\gamma)}^{(\beta)}(\tau) \rho_{m(\gamma),N}(t) + I_{N,N}^{(\beta)}(\tau) \rho_{N,N}(t), \end{aligned} \quad (13)$$

where

$$\begin{aligned} I_{n(\beta),m(\gamma)}^{(\beta)}(\tau) &= \sum_I (e^{iH\tau})_{n(\beta),I(\beta)} (e^{-iH\tau})_{I(\beta),m(\gamma)}, \\ I_{N,m(\gamma)}^{(\beta)}(\tau) &= \sum_I (e^{iH\tau})_{N,I(\beta)} (e^{-iH\tau})_{I(\beta),m(\gamma)}, \end{aligned} \quad (14)$$

$$I_{N,N}^{(\beta)}(\tau) = \sum_I |(e^{iH\tau})_{N,I(\beta)}|^2.$$

Equation (13) contains diagonal contributions, which

represent level populations, as well as off-diagonal terms, which account for coherence effects. Van Hove^{34a} has reduced formally equivalent expressions to a diagonal form by invoking the random phase approximation for the amplitudes $a_{I(\beta)}(t)$. However, Van Hove's diagonal singularity condition^{34a} as well as Zwanzig's weak coupling theory^{34b} rest on the notion of "smooth" coupling, where the coupling terms V exhibit weak energy dependence. Such an approach does not apply for the RRCM. Instead, we assert that as a consequence of the randomness of the radiative coupling terms the off-diagonal interference functions in Eq. (14) vanish and only the diagonal terms survive. This is essentially Kay's assumption,⁴⁶ which we adopt for the RRCM. To provide a justification for this ansatz we utilize the conventional expansion of the time evolution operator for the system characterized by $H = H_0 + V$,

$$e^{-iH\tau} = e^{-iH_0\tau} - i \int_0^\tau dt_1 e^{-H_0\tau(\tau-t_1)} V e^{-iHt_1}. \quad (15)$$

It is now a straightforward matter to verify that Eqs. (5)–(7) imply that all the contributions to Eq. (14) of the form $VA(\alpha)V$, $VA(\alpha)VA(\beta)VA(\gamma)V$, etc., which contain an even number of the radiative coupling terms V , are diagonal. For terms which contain an odd number of V terms, e.g., $VA(\alpha)VA(\beta)V$, we have to invoke an additional cancellability assumption, or rather rely on the mutual cancellation of these odd V , off-diagonal contributions. The RRCM now results in the diagonal contributions to Eq. (14)

$$\begin{aligned} I_{n(\beta),m(\gamma)}^{(\beta)}(\tau) &= I_{m(\gamma),m(\gamma)}^{(\beta)}(\tau) \delta_{nm} \delta_{\gamma\beta}, \\ I_{N,m(\gamma)}^{(\beta)}(\tau) &= 0. \end{aligned} \quad (14')$$

Thus Eq. (13) assumes the form of a generalized master equation

$$P_{(\beta)}(t + \tau) = \sum_m \sum_\gamma \rho_{m(\gamma),m(\gamma)}(t) \gamma_{m(\gamma)-(\beta)}(\tau) + \rho_{N,N}(t) \gamma_{N-(\beta)}(\tau), \quad (16)$$

where

$$\gamma_{m(\gamma)-(\beta)}(\tau) = \sum_I |(e^{-iH\tau})_{m(\gamma),I(\beta)}|^2, \quad (17a)$$

$$\gamma_{N-(\beta)}(\tau) = \sum_I |(e^{-iH\tau})_{N,I(\beta)}|^2, \quad (17b)$$

are the total probabilities for the transitions during the time interval τ from the state $|m(\gamma)\rangle$ to the β manifold and from the state $|N\rangle$ to the β manifold, respectively. As we consider now a system consisting of the $|N\rangle$ state and the set of quasicontinua $\{|I(\beta)\rangle\}$ ($\beta = 1 \cdots Q$), Eq. (17) now obeys the unitarity conditions

$$\begin{aligned} \sum_{\beta=1}^Q \gamma_{m(\gamma)-(\beta)}(\tau) + |\langle m(\gamma) | e^{-iH\tau} | N \rangle|^2 &= 1, \\ \sum_{\beta=1}^Q \gamma_{N-(\beta)}(\tau) + |\langle N | e^{-iH\tau} | N \rangle|^2 &= 1, \end{aligned} \quad (18)$$

which reveals that the basic probability conservation law

$$\sum_{\beta=1}^Q P_{(\beta)}(t + \tau) + P_N(t + \tau) = 1 \quad (19)$$

is preserved, demonstrating that the RRCM is self-consistent.

To recast the master equation (16) in a more transparent form we can approximate the probabilities to second order in terms of the golden rule rates

$$\gamma_{N \rightarrow \{\beta\}}(\tau) = \Gamma [N \rightarrow \{\beta\}] \tau, \quad (20a)$$

$$\gamma_{m(\gamma) \rightarrow \{\beta\}}(\tau) = \Gamma [m(\gamma) \rightarrow \{\beta\}] \tau, \quad (20b)$$

$$\Gamma [m(\gamma) \rightarrow \{\beta\}] = 2\pi \sum_I |V_{m(\gamma), I(\beta)}|^2 \delta(E_{m(\gamma)} - E_{I(\beta)}), \quad (21a)$$

$$\Gamma [N \rightarrow \{\beta\}] = 2\pi \sum_I |V_{N, I(\beta)}|^2 \delta(E_N - E_{I(\beta)}). \quad (21b)$$

This second-order expansion is expected to be valid for a quasicontinuum provided that $\tau \ll \langle \rho_\beta \rangle$ and $\Gamma \gg \langle \rho_{\{\beta\}} \rangle^{-1}$, where $\langle \rho_{\{\beta\}} \rangle$ is an average density of states in the $\{|I(\beta)\rangle\}$ manifold. Expanding the lhs of Eq. (16), utilizing Eqs. (18), (20), and (21), and disregarding a small back-transfer contribution [which is of the order of $1/n$, n being the number of $\{\beta\}$ quasicontinuum states] now results in a conventional master equation

$$\begin{aligned} \frac{\partial P_{\{\beta\}}(t)}{\partial t} = & \sum_m \sum_\gamma \Gamma [m(\gamma) \rightarrow \{\beta\}] \rho_{m(\gamma), m(\gamma)}(t) \\ & - \sum_I \sum_\gamma \Gamma [I(\beta) \rightarrow \{\gamma\}] \rho_{I(\beta), I(\beta)}(t) \\ & + \Gamma [N \rightarrow \{\beta\}] \rho_{N, N}(t). \end{aligned} \quad (22)$$

Equation (22) provides us with a set of kinetic equations. To bring these equations into a manageable form we shall invoke a coarse-graining hypothesis for the decay widths in Eq. (21). We assume that these widths are independent of the particular initial states. Bearing in mind that the delta functions appearing in Eq. (21) are introduced in the case of a discrete spectrum only for bookkeeping purposes, we shall express the coarse-grained widths in terms of the densities of states $\rho_{\{\beta\}}$ in the quasicontinua. Introducing the explicit form of the radiative interactions, Eq. (3c), the intercontinuum coupling prevails between adjacent quasicontinua and the relevant terms are

$$\begin{aligned} K_{\beta \rightarrow \beta \pm 1} = & \langle \Gamma [I(\beta) \rightarrow \{\beta \pm 1\}] \rangle \\ = & 2\pi \langle |\mu_{I(\beta), I(\beta \pm 1)}|^2 \rho_{\{\beta \pm 1\}} \rangle \epsilon^2. \end{aligned} \quad (23)$$

Finally we set

$$\Gamma_N = \langle \Gamma [N \rightarrow \{\beta\}] \rangle, \quad (24)$$

where Γ_N is given by Eq. (9). The averaging $\langle \rangle$ in Eqs. (23) and (24) is performed over final states.

Replacing the microscopic widths in Eq. (22) by the average values and utilizing Eq. (18), we obtain the following set of birth and death kinetic equations:

$$\begin{aligned} \dot{P}_{(1)} = & \Gamma_N P_N - K_{1-2} P_{(1)} + K_{2-1} P_{(2)}, \\ \dot{P}_{(2)} = & K_{1-2} P_{(1)} + K_{3-2} P_{(3)} - (K_{2-3} + K_{2-1}) P_{(2)}, \\ & \vdots \\ \dot{P}_{(\beta)} = & K_{\beta-1-\beta} P_{(\beta-1)} + K_{\beta+1-\beta} P_{(\beta+1)} \\ & - (K_{\beta-\beta+1} + K_{\beta-\beta-1}) P_{(\beta)}, \quad \beta = 2 \cdots Q-1. \end{aligned} \quad (25)$$

Finally, we shall briefly consider the dissociation in range III. We adopt the NJR sequential decay model⁴⁴ assigning to each level in the highest $\{|I(Q)\rangle\}$ manifold a constant independent decay width

$$K_D = 2\pi |W(c, I(Q))|^2 \rho_c, \quad (26)$$

where ρ_c is the (average) density of states in the dissociative channel. The time evolution of the population of the $\{|I(Q)\rangle\}$ manifold is characterized by the irreversible decay

$$\dot{P}_{(Q)} = K_{Q-1-Q} P_{(Q-1)} - K_{Q-Q-1} P_{(Q)} - K_D P_{(Q)}. \quad (27)$$

The population of the decay channel $P_{(c)} = \sum_c |a_c(t)|^2$, where $a_c(t)$ is defined by Eq. (1), is now governed by the simple equation

$$\dot{P}_{(c)} = K_D P_{(Q)}. \quad (28)$$

III. RESULTS

To summarize, let us express the time evolution of the system in a concise manner. In range I we get the effective Hamiltonian equation for the amplitudes

$$i \dot{\mathbf{a}}(t) = \mathbf{H}_{\text{eff}} \mathbf{a}(t), \quad (29)$$

where

$$\mathbf{a}(t) = \begin{pmatrix} a_1(t) \\ a_2(t) \\ \vdots \\ a_N(t) \end{pmatrix}, \quad (30)$$

$$(\mathbf{H}_{\text{eff}})_{\alpha, \alpha} = E(\alpha) - \frac{i}{2} \Gamma_N \delta_{\alpha, N}, \quad (30')$$

$$(\mathbf{H}_{\text{eff}})_{\alpha, \beta} = \mu_{\alpha, \beta} \delta_{\alpha, \beta \pm 1} \epsilon. \quad (30'')$$

In range II the populations are given by

$$\dot{\mathbf{P}}(t) = \mathbf{S}(t) + \mathbf{K} \mathbf{P}(t), \quad (31)$$

where

$$\mathbf{P}(t) = \begin{pmatrix} P_1(t) \\ P_2(t) \\ \vdots \\ P_Q(t) \end{pmatrix} \quad (31')$$

is the vector of the populations; the feeding vector is

$$\mathbf{S}(t) = \begin{pmatrix} \Gamma_N P_N(t) \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad (31'')$$

where $P_N(t)$ is obtained from the solution of Eq. (30). Finally, the kinetic matrix is

$$K = \begin{pmatrix} -K_{1-2} & 0 & 0 & 0 & \dots & 0 \\ K_{1-2} & -(K_{2-3} + K_{2-1}) & K_{3-2} & 0 & \dots & 0 \\ 0 & K_{2-3} & -(K_{3-4} + K_{3-2}) & K_{4-3} & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & 0 & 0 & \dots & -(K_{Q-Q-1} + K_D) \end{pmatrix}. \quad (31''')$$

In range III, Eq. (28) determines the population rate of the true dissociative channel so that the photodissociation probability during the pulse is

$$W_1 = K_D \int_0^T P_{(Q)}(t) dt, \quad (32a)$$

while the probability for photofragmentation after the termination of the pulse is

$$W_2 = P_{(Q)}(T), \quad (32b)$$

where the population $P_{(Q)}(t)$ is obtained from the solution of Eq. (31).

Equations (30)–(32) constitute the final results of the RRCM. The following conclusions emerge:

(a) All the features of the coherent excitation in range I (see Sec. I) are preserved.

(b) The effective Hamiltonian formalism for range I is applicable only within the framework of the RRCM.

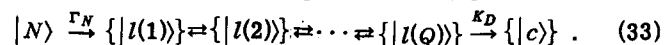
(c) The “leaking” from range I to range II is determined by the transition probability Γ_N , Eq. (9), which is proportional to ϵ^2 , i.e., to the laser intensity I . The concept of the leakage into the quasicontinuum was originally advanced by Letokhov and Makarov.²⁸

(d) The dependence $\Gamma_N \propto I$ raises the definite possibility of damping of the coherent excitation in range I at high laser intensities. Utilizing the analysis of Eberly and Ackerhalt⁵⁰ we note that when (a) Γ_N exceeds all the Rabi frequencies and (b) Stark shifts compensate for the energy defects, coherence effects in range I will be eroded. This situation will prevail near saturation of the leaking from range I to range II. Then the necessary condition is $\Gamma_N \gg \mu_{\alpha-\alpha+1}\epsilon$ for all α . As $\Gamma_N \propto \epsilon^2$ and the Rabi frequency is determined by ϵ , it is possible, at least in principle, to achieve erosion of coherence effects in range I at high intensities. Only then can region I be treated also in terms of a master equation.

(e) The time evolution of the populations in range II is described in terms of a conventional kinetic master equation. Random coupling is sufficient to erode all coherence effects in range II.

(f) The rates $K_{\beta-\beta+1}$ for excitation in range II are proportional to the laser intensity. Thus excitation in range II will be essentially determined by the laser energy, i.e., $\epsilon^2 T$, rather than by the laser power.

(g) The kinetic equations in range II correspond to the simple reversible sequential decay process



(h) In the first stage of the sequence (33), $|N\rangle$

– $\{|I(1)\rangle\}$ induced by the radiative coupling Γ_N the decay of the single $|N\rangle$ state to the $\{|I(1)\rangle\}$ dense manifold is practically irreversible on the time scale of the experiment³¹ and no stimulated emission, which is analogous to the reversible $\{|I(1)\rangle\} \rightarrow |N\rangle$ process, is expected to be exhibited.

(i) The radiative coupling between adjacent quasicontinua results in reversible absorption and stimulated emission which can be described as reversible process. The self-consistent treatment of the RRCM model presented herein concurs with the relation proposed by Black *et al.*¹⁵ Obviously, we are concerned here with “long time” excitation of the quasicontinuum disregarding interesting, time-resolved, transient effects.

(j) The RRCM model opens some interesting possibilities for the theoretical study of medium perturbations in multiphoton photodissociation. Medium effects fall in general into two categories: (1) Phase destruction processes, and (2) population modifications. At low pressures of an “inert” gas (excluding $V-V$ transfer) phase destructive collisions dominate and range I can then be treated in terms of population rate equations for a discrete manifold which involve absorption and stimulated emission, while the behavior of range II is practically unmodified before effective vibrational deactivation sets in. When medium effects at higher pressures are considered the effects of vibrational relaxation in both ranges I and II have to be incorporated. This open problem of medium induced population changes is of considerable interest in relation to the recent observation of multiphoton photodissociation of a guest molecule in a rare-gas solid.⁵¹

IV. CONCLUDING REMARKS

What is significant from the point of view of general methodology is that the RRCM provides the first step towards a self-consistent microscopic theory underlying collisionless excitations of a molecular manifold, which rests on the notion of the genuine (although unknown) molecular level structure, evading dangerous and not well-defined issues such as IVR. In particular, we have demonstrated that random radiative coupling in a congested level structure can result in erosion of coherence effects, without alluding to the notion of intramolecular T_2 -type processes. The RRCM constitutes a theory which attempts to provide physical insight, on the basis of minimal physical information, and which will hopefully be useful in correlating a variety of experimental data for multiphoton photofragmentation of large molecules. It is important to emphasize at this point that the RRCM is applicable for the study of large molecules. Indeed, the “transition” from range I to range II bears

a close analogy to the transition from the small molecule case to the statistical limit in the theory of electronic relaxation.³¹ The onset of range II is essentially determined by the size of the molecule, i.e., the number of atoms, as well as by the excess vibrational energy. Obviously, for a diatomic molecule range II does not exist. For triatomics it is an open question whether range II exists at all and, in any case, range I will contain a large number of levels and the properties of range I will dominate the characteristics of the multiphoton excitation process. In large molecules like SF₆ the onset of range II is low and for such molecules the coarse-graining procedure inherent in the RRCM is physically acceptable. Finally, it should be noted that the RRCM makes possible the accessibility of electronically excited configurations, so that electronically excited levels of the parent molecule or electronically excited fragments may be produced.

ACKNOWLEDGMENTS

We are grateful to A. Nitzan and B. Carmeli for many stimulating discussions.

- ¹N. R. Isenor and M. R. Richardson, *Appl. Phys. Lett.* **18**, 225 (1971).
- ²N. R. Isenor, V. Merchant, R. S. Hallsworth, and M. C. Richardson, *Can. J. Phys.* **51**, 1281 (1973).
- ³R. V. Ambartsumyan, V. S. Letokhov, E. A. Ryabov, and N. V. Chekalin, *JETP Lett.* **20**, 272 (1975).
- ⁴R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, *JETP Lett.* **21**, 171 (1975).
- ⁵R. V. Ambartsumyan, N. V. Chekalin, V. S. Letokhov, and E. A. Ryabov, *Chem. Phys. Lett.* **36**, 301 (1975).
- ⁶R. V. Ambartsumyan, N. V. Chekalin, V. S. Doljikov, V. S. Letokhov, and E. A. Ryabov, *Chem. Phys. Lett.* **25**, 515 (1974).
- ⁷J. L. Lyman, R. J. Jensen, J. Rink, C. P. Robinson, and S. D. Rockwood, *Appl. Phys. Lett.* **27**, 87 (1975).
- ⁸C. P. Robinson, *Proc. Laser Spectrosc. Conf.*, 2nd, Megeve, (1975).
- ⁹K. L. Kompa, in *Tunable Lasers and Applications*, edited by A. Mooradian, T. Yaeger, and P. Stokseth (Springer, Heidelberg, 1976).
- ¹⁰J. D. Campbell, G. Hancock, and K. H. Welge, *Chem. Phys. Lett.* **43**, 581 (1976).
- ¹¹P. Kolodner, C. Winterfeld, and E. Yablonovitch, *Opt. Commun.* **20**, 119 (1977).
- ¹²M. J. Coggiola, P. A. Schultz, Y. T. Lee, and Y. R. Shen, *Phys. Rev. Lett.* **38**, 17 (1977).
- ¹³(a) R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puretskii, *JETP Lett.* **23**, 22 (1976); (b) R. V. Ambartsumyan, N. P. Furzikov, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, and A. A. Puretskii, *Opt. Commun.* **18**, 517 (1976); (c) R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, G. N. Makarov, A. A. Puretskii, and N. P. Furzikov, *JETP Lett.* **23**, 195 (1976); (d) V. N. Bagratashvili, I. N. Knyazev, V. S. Letokhov, and V. V. Lobko, *Opt. Commun.* **18**, 525 (1976).
- ¹⁴Z. Karni, A. Gupta, R. N. Zare, S. T. Lin, J. Nieman, and A. Ron, *Chem. Phys. Lett.* (in press).
- ¹⁵J. G. Black, E. Yablonovitch, N. Bloembergen, and S. Mukamel, *Phys. Rev. Lett.* **38**, 1131 (1977).
- ¹⁶E. R. Grant, P. A. Schultz, A. S. Sudbo, M. J. Coggiola, Y. R. Shen, and Y. T. Lee, in *Multiphoton Processes*, edited by J. H. Eberly and P. Lampropoulos (Wiley, New York, 1978), p. 359.
- ¹⁷N. Bloembergen and E. Yablonovitch, *Physics Today* **31**, 23 (1978).
- ¹⁸N. Bloembergen, *Opt. Commun.* **15**, 416 (1975).
- ¹⁹(a) M. F. Goodman and E. Thiele, *Phys. Rev. A* **5**, 1358 (1972); (b) J. Stone, E. Thiele, and M. F. Goodman, *J. Chem. Phys.* **59**, 2909 (1973); *ibid.* **63**, 2936 (1975). (c) M. F. Goodman, J. Stone, and E. Thiele, *J. Chem. Phys.* **59**, 2919 (1973); *ibid.* **63**, 2936 (1975).
- ²⁰D. M. Larsen and N. Bloembergen, *Opt. Commun.* **17**, 254 (1976).
- ²¹F. H. M. Faisal, *Opt. Commun.* **17**, 247 (1976).
- ²²(a) S. Mukamel and J. Jortner, *Chem. Phys. Lett.* **40**, 150 (1976); (b) S. Mukamel and J. Jortner, *J. Chem. Phys.* **65**, 5204 (1976).
- ²³T. P. Cotter, W. Fuss, K. L. Kompa, and H. Stafast, *Opt. Commun.* **18**, 220 (1976).
- ²⁴N. Bloembergen, C. D. Cantrell, and D. M. Larsen, *Ref.* **9**, p. 162.
- ²⁵D. M. Larsen, *Opt. Commun.* **19**, 404 (1976).
- ²⁶(a) V. S. Letokhov and A. A. Makarov, *Opt. Commun.* **17**, 250 (1976); (b) V. S. Letokhov and A. A. Makarov, *Appl. Phys.* **16**, 47 (1978).
- ²⁷(a) M. F. Goodman, J. Stone, and D. A. Dows, *J. Chem. Phys.* **65**, 5052 (1976); (b) M. F. Goodman, J. Stone, and D. A. Dows, *J. Chem. Phys.* **65**, 5062 (1976).
- ²⁸(a) C. D. Cantrell and H. W. Galbraith, *Opt. Commun.* **18**, 513 (1976); (b) C. D. Cantrell and H. W. Galbraith, *Opt. Commun.* **21**, 374 (1977).
- ²⁹V. I. Gorchakov and V. N. Sazanov, *JETP Lett.* **43**, 241 (1976).
- ³⁰C. D. Cantrell, W. H. Galbraith, and J. R. Ackerhalt in *Ref.* **16**, p. 331.
- ³¹(a) M. Bixon and J. Jortner, *J. Chem. Phys.* **50**, 3284 (1969); (b) J. Jortner and S. Mukamel, in *The World of Quantum Chemistry*, edited by R. Daudel and B. Pullman (Reidel, Holland, 1973), p. 145; (c) J. Jortner and S. Mukamel, in *International Review of Science, Physical Chemistry Series Two, Vol. 1, Theoretical Chemistry*, edited by A. D. Buckingham and C. A. Coulson (Butterworths, London, 1975), p. 391.
- ³²S. Mukamel (private communication).
- ³³D. P. Hodgkinson and J. S. Briggs, *Chem. Phys. Lett.* **43**, 451 (1976).
- ³⁴(a) L. Van Hove, *Physica (Utrecht)* **21**, 517 (1955); (b) R. Zwanzig, *J. Chem. Phys.* **33**, 1338 (1960); (c) R. Zwanzig, *Lectures in Theoretical Physics III* (Interscience, New York, 1961), p. 106.
- ³⁵R. L. Swofford, M. E. Long, and A. C. Albrecht, *J. Chem. Phys.* **65**, 179 (1976).
- ³⁶J. Jortner, *Proc. Soc. Photo-Opt. Instrum. Eng.* **113**, 88 (1977).
- ³⁷R. Haroche, *Ann. Phys. (Paris)* **6**, 189 (1971).
- ³⁸C. Cohen Tannoudji, in *Cargese Lectures in Physics*, Vol. 2 (Gordon and Breach, London, 1967).
- ³⁹S. A. Rice, I. McLaughlin, and J. Jortner, *J. Chem. Phys.* **49**, 2756 (1968).
- ⁴⁰R. Lefebvre and J. A. Beswick, *Mol. Phys.* **23**, 1223 (1972).
- ⁴¹A. Nitzan, J. Jortner, and B. J. Berne, *Mol. Phys.* **26**, 281 (1973).
- ⁴²O. Atabek, J. A. Beswick, R. Lefebvre, S. Mukamel, and J. Jortner, *J. Chem. Phys.* **65**, 4035 (1976).
- ⁴³J. A. Beswick and J. Jortner, *Chem. Phys. Lett.* **49**, 13 (1977).
- ⁴⁴A. Nitzan, J. Jortner, and P. M. Rentzepis, *Mol. Phys.* **22**, 585 (1971).
- ⁴⁵E. J. Heller and S. A. Rice, *J. Chem. Phys.* **61**, 936 (1974).
- ⁴⁶K. G. Kay, *J. Chem. Phys.* **61**, 5205 (1974).
- ⁴⁷C. Tric, "Intramolecular vibrational redistribution," Preprint.
- ⁴⁸B. Carmeli and A. Nitzan, *Chem. Phys. Lett.* (in press).
- ⁴⁹The failure of the technique advocated in Ref. 36 can be demonstrated by considering parallel decay of a single discrete state into a pair of coupled continua.
- ⁵⁰J. R. Ackerhalt and J. H. Eberly, *Phys. Rev. A* **14**, 1705 (1976).
- ⁵¹R. V. Ambartsumyan, Yu. A. Gorokhov, G. N. Makarov, A. A. Puretskii, and N. P. Furzikov, *JETP Lett.* **24**, 257 (1976).